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## The riverine source of CH<sub>4</sub> and N<sub>2</sub>O from the Republic of Congo, western Congo Basin

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**Abstract.** We discuss concentrations of dissolved CH<sub>4</sub>, N<sub>2</sub>O, O<sub>2</sub>, NO<sub>3</sub><sup>−</sup> and NH<sub>4</sub><sup>+</sup>, and emission fluxes of CH<sub>4</sub> and N<sub>2</sub>O for river sites in the western Congo Basin, Republic of Congo (ROC). Savannah, swamp forest and tropical forest samples were collected from the Congo main stem and seven of its tributaries during November 2010 (41 samples; “wet season”) and August 2011 (25 samples; “dry season”; CH<sub>4</sub> and N<sub>2</sub>O only). Dissolved inorganic nitrogen (DIN: NH<sub>4</sub><sup>+</sup> + NO<sub>3</sub><sup>−</sup>; wet season) was dominated by NO<sub>3</sub><sup>−</sup> (63 ± 19 % of DIN). Total DIN concentrations (1.5–45.3 μmol L<sup>−1</sup>) were consistent with the near absence of agricultural, domestic and industrial sources for all three land types. Dissolved O<sub>2</sub> (wet season) was mostly undersaturated in swamp forest (36 ± 29 %) and tropical forest (77 ± 36 %) rivers but predominantly supersaturated in savannah rivers (100 ± 17 %). The dissolved concentrations of CH<sub>4</sub> and N<sub>2</sub>O were within the range of values reported earlier for sub-Saharan African rivers. Dissolved CH<sub>4</sub> was found to be supersaturated (11.2–9553 nmol L<sup>−1</sup>; 440–354 444 %), whereas N<sub>2</sub>O ranged from strong undersaturation to supersaturation (3.2–20.6 nmol L<sup>−1</sup>; 47–205 %). Evidently, rivers of the ROC are persistent local sources of CH<sub>4</sub> and can be minor sources or sinks for N<sub>2</sub>O. During the dry season the mean and range of CH<sub>4</sub> and N<sub>2</sub>O concentrations were quite similar for the three land types. Wet and dry season mean concentrations and ranges were not significant for N<sub>2</sub>O

for any land type or for CH<sub>4</sub> in savannah rivers. The latter observation is consistent with seasonal buffering of river discharge by an underlying sandstone aquifer. Significantly higher wet season CH<sub>4</sub> concentrations in swamp and forest rivers suggest that CH<sub>4</sub> can be derived from floating macrophytes during flooding and/or enhanced methanogenesis in adjacent flooded soils. Swamp rivers also exhibited both low (47 %) and high (205 %) N<sub>2</sub>O saturation but wet season values were overall significantly lower than in either tropical forest or savannah rivers, which were always supersaturated (103–266 %) and for which the overall means and ranges of N<sub>2</sub>O were not significantly different. In swamp and forest rivers O<sub>2</sub> saturation co-varied inversely with CH<sub>4</sub> saturation (log %) and positively with % N<sub>2</sub>O. A significant positive correlation between N<sub>2</sub>O and O<sub>2</sub> saturation in swamp rivers was coincident with strong N<sub>2</sub>O and O<sub>2</sub> undersaturation, indicating N<sub>2</sub>O consumption during denitrification in the sediments. In savannah rivers persistent N<sub>2</sub>O supersaturation and a negative correlation between N<sub>2</sub>O and O<sub>2</sub> suggest N<sub>2</sub>O production mainly by nitrification. This is consistent with a stronger correlation between N<sub>2</sub>O and NH<sub>4</sub><sup>+</sup> than between N<sub>2</sub>O and NO<sub>3</sub><sup>−</sup>. Our ranges of values for CH<sub>4</sub> and N<sub>2</sub>O emission fluxes (33–48 705 μmol CH<sub>4</sub> m<sup>−2</sup> d<sup>−1</sup>; 1–67 μmol N<sub>2</sub>O m<sup>−2</sup> d<sup>−1</sup>) are within the ranges previously estimated for sub-Saharan African rivers but they include uncertainties deriving from our use of “basin-wide” values for CH<sub>4</sub> and N<sub>2</sub>O

gas transfer velocities. Even so, because we did not account for any contribution from ebullition, which is quite likely for CH<sub>4</sub> (at least 20 %), we consider our emission fluxes for CH<sub>4</sub> to be conservative.

## 1 Introduction

Methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) accounted for 17 and 6 %, respectively, of the total atmospheric radiative forcing by well-mixed greenhouse gases in 2011 (Myhre et al., 2013). CH<sub>4</sub> also impacts tropospheric oxidising capacity, O<sub>3</sub> and OH radical and is a source of stratospheric O<sub>3</sub> (Myhre et al., 2013), while N<sub>2</sub>O is the largest cause of stratospheric O<sub>3</sub> loss, via NO production (Ravishankara et al., 2009). Since the onset of the industrial revolution, tropospheric CH<sub>4</sub> and N<sub>2</sub>O have substantially increased but their growth rates have varied. The early 1980s to the mid-2000s saw an overall decline in tropospheric CH<sub>4</sub> growth (Dlugokencky et al., 2009, 2011). This has been ascribed to declining fossil fuel emissions and/or variations in the OH radical sink (Rice et al., 2016; Schaefer et al., 2016), punctuated by episodic events such as the 1991–1992 Pinatubo eruption and an intense 1997–1998 El Niño (Nisbet et al., 2016). However, since 2007 increased growth has been sustained. Recent evidence from isotopic studies (Nisbet et al., 2016) and a box model (Schaefer et al., 2016) ascribes this to increased biogenic emissions, particularly in the tropics, where they have been linked to expanding tropical wetlands in response to positive rainfall anomalies (Nisbet et al., 2016), and/or growing emissions from agricultural sources (Schaefer et al., 2016). The mean CH<sub>4</sub> tropospheric dry mole fraction in 2011,  $1803 \pm 2$  ppbv, was 150 % above the pre-industrial value (Hartmann et al., 2013). Of particular note for N<sub>2</sub>O, the availability of sufficiently reliable data on the anthropogenic components of river, estuary and coastal zone sources resulted in their classification being changed in the IPCC AR4 synthesis, from “natural” to “anthropogenic” (Denman et al., 2007). A small but significant seasonal to inter-annual variability in N<sub>2</sub>O growth rate may reflect climate-driven changes in soil N<sub>2</sub>O (Thompson et al., 2013). The current rate of N<sub>2</sub>O growth is  $0.73 \pm 0.03$  ppb yr<sup>-1</sup> and its tropospheric dry mole fraction in 2011,  $324 \pm 0.1$  ppbv, was ~20 % above its pre-industrial value (Hartmann et al., 2013).

The evidence base for freshwater ecosystems (streams, rivers, lakes, and reservoirs) as important tropospheric CH<sub>4</sub> and N<sub>2</sub>O sources is small but increasing. The global freshwater CH<sub>4</sub> source could be  $\sim 10^{13}$ – $10^{14}$  g yr<sup>-1</sup> (Bastviken et al., 2011; Kirschke et al., 2013; Stanley et al., 2016). This order of magnitude range largely reflects a discrepancy between “top-down” approaches based on atmospheric inversions (e.g. Kirschke et al., 2013) and “bottom-up” estimates that necessitate the upscaling of freshwater observations (e.g. Bastviken et al., 2011). For example, atmospheric

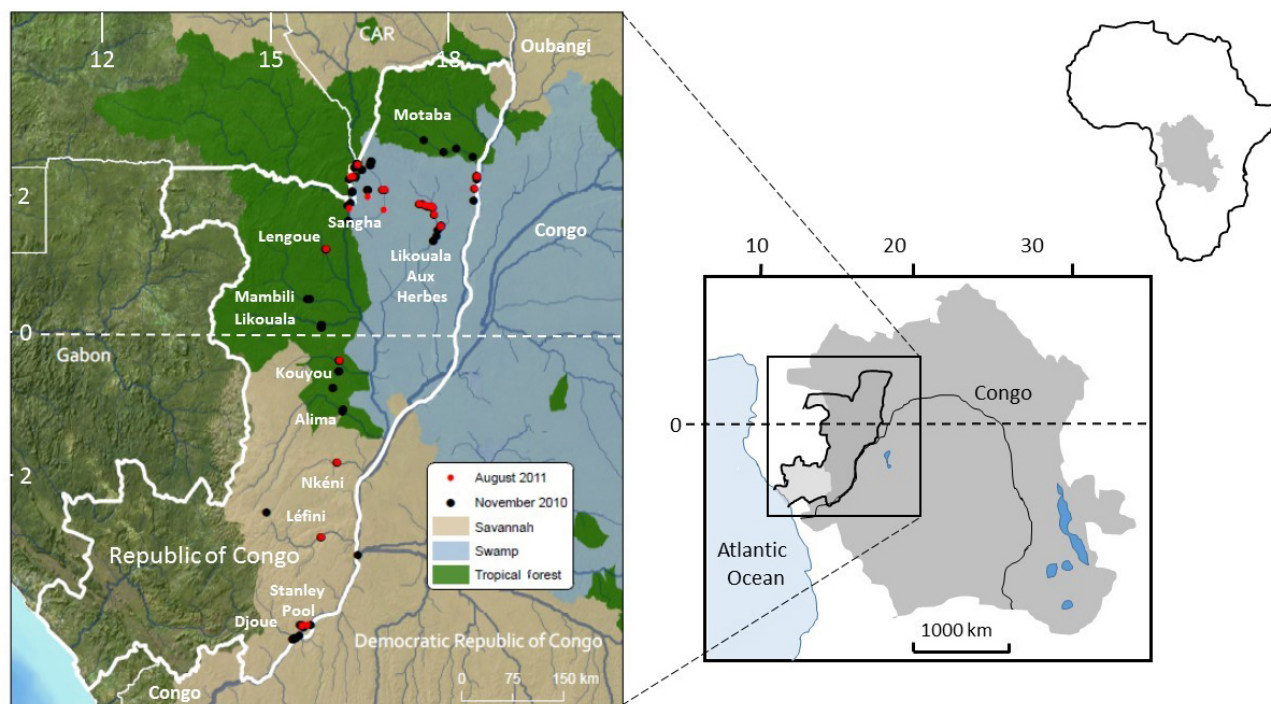
constraints on top-down budgets imply that some component emissions of bottom-up approaches may be overestimates (Saunois et al., 2016). Notwithstanding this uncertainty, the global freshwater CH<sub>4</sub> source can be evaluated in the light of natural and total global CH<sub>4</sub> source estimates of  $179$ – $484 \times 10^{12}$  and  $526$ – $852 \times 10^{12}$  g yr<sup>-1</sup> respectively (Kirschke et al., 2013). Quantifying the global freshwater contribution thus has high inherent uncertainty but based on these estimates it could be ~2–56 % of natural CH<sub>4</sub> emissions and ~1–19 % of total CH<sub>4</sub> emissions. Converting these to CO<sub>2</sub> equivalents based on a 100-year global warming potential gives  $\sim 0.65 \times 10^{15}$  g C (CO<sub>2</sub> equivalent) yr<sup>-1</sup> (Bastviken et al., 2011), a significant offset to the combined terrestrial and oceanic carbon sink  $\sim 5.5 \times 10^{15}$  g C yr<sup>-1</sup> (Le Quéré et al., 2015). A global estimate of river N<sub>2</sub>O emissions based on microbial production from agriculturally-derived nitrogen is  $\sim 6.8 \times 10^{11}$  g yr<sup>-1</sup>, around 10 % of the total global anthropogenic N<sub>2</sub>O source, but because this involved upscaling emissions from entirely within the contiguous United States (Beaulieu et al., 2011), it too must be highly uncertain.

Tropical river systems in Africa include some of the world’s largest, together contributing ~12 % of both global freshwater discharge (Valentini et al., 2014) and river surface area (Raymond et al., 2013). Borges et al. (2015b) recently reported annual emissions  $\sim 3$ – $4 \times 10^{12}$  g CH<sub>4</sub> and  $\sim 10^{10}$  g N<sub>2</sub>O for 12 large river systems in sub-Saharan Africa, including the three largest by catchment area (Congo, Niger, Zambezi). Notably, their CH<sub>4</sub> estimate is 5 times higher than was previously attributed to all tropical rivers (Bastviken et al., 2011) and both estimates are significant at the continental scale given that reported total African emissions are  $\sim 66 \pm 35 \times 10^{12}$  g CH<sub>4</sub> yr<sup>-1</sup> and  $3.3 \pm 1.3 \times 10^{12}$  g N<sub>2</sub>O yr<sup>-1</sup> (Valentini et al., 2014).

The potential scale of CH<sub>4</sub> and N<sub>2</sub>O emissions from tropical freshwaters and their attendant uncertainties warrant further investigation. In this paper we present and discuss concentrations of dissolved CH<sub>4</sub>, N<sub>2</sub>O, O<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, and corresponding CH<sub>4</sub> and N<sub>2</sub>O emissions for river sites in savanna, swamp forest and tropical forest. Samples were collected along the Congo main stem and in seven of its tributary systems in the western Congo Basin, Republic of Congo, during November 2010 and August 2011.

## 2 Study site and sample locations

The ~4700 km long Congo River (Fig. 1) has an equatorial location that affords it a bimodal hydrological regime. Maximal flows are in December and May and minimal flows are in August and March (Coyne et al., 2005). The Congo Basin (9° N–14° S, 11–31° E) is the largest hydrological system in Central Africa, covering  $\sim 3.8 \times 10^6$  km<sup>2</sup> (~12 % of the total African land mass; Fig. 1) and incorporating the world’s fourth largest wetland area  $\sim 3.6 \times 10^5$  km<sup>2</sup> (La-



**Figure 1.** Locations of river sampling stations in the Republic of Congo.

porte et al., 1998). The Congo's annual freshwater discharge is the world's second largest at  $\sim 1300 \text{ km}^3$  (Borges et al., 2015b), 50 % of all freshwater flow from Africa to the Atlantic Ocean. Rivers and streams in the Congo Basin have a total open water surface area  $\sim 2.7 \times 10^4 \text{ km}^2$  (Raymond et al., 2013). The climate is warm (mean annual temperature  $24.8 \pm 0.8^\circ \text{C}$ ) and humid with an annual rainfall  $\sim 1800 \text{ mm}$  (Laraque et al., 2001).

We sampled the Congo main stem, seven of its tributary rivers and some of their sub-tributaries, at sites within the Republic of Congo (ROC: area  $3.4 \times 10^5 \text{ km}^2$ ), in the western Congo Basin (Fig. 1). Individual catchment areas, freshwater discharge rates and rainfall are listed in Table 1. Around 50 % of the ROC land area is classified as tropical forest, with the remainder classified as either swamp or savannah in approximately equal proportion (Clark and Decalo, 2012). Sampling sites were selected to represent each of these three land cover types (Fig. 1), which were georeferenced to the World Geodetic System 1984 (WGS84) and intersected with the highest level sub-watershed polygons defined by the HYDRO1K global hydrological data set (US Geological Survey, 2000). This enabled assigning the fractional cover for each land cover type, and hence the dominant land cover type, to the areas immediately surrounding each sampling location. Swamp includes both temporally and permanently inundated areas of “forest”, with vegetation adapted to poorly drained, anaerobic soils (Mayaux et al., 2002). For all three land cover types the mean annual temperature range (period 1990–2012) is  $\sim 1$ –

$3^\circ \text{C}$ . Temperatures are lowest ( $\sim 22$ – $24^\circ \text{C}$ ) in July–August and highest ( $\sim 25$ – $26^\circ \text{C}$ ) in March–April (<http://sdwebx.worldbank.org/climateportal/>). For savannah the average monthly rainfall during July–May (1990–2012) is  $\sim 120$ – $260 \text{ mm}$ , typically being maximal in October–November, but  $< 40 \text{ mm}$  falls during June–August (<http://sdwebx.worldbank.org/climateportal/>). For forest and swamp the annual range in monthly rainfall is less pronounced. Both have two discernable rainfall maxima, during April–May and October–November ( $\sim 150$ – $240 \text{ mm month}^{-1}$ ), and a minimum in June–August ( $\sim 40$ – $120 \text{ mm month}^{-1}$ ) (<http://sdwebx.worldbank.org/climateportal/>).

ROC swamp and forest (Fig. 1) broadly correspond to the westernmost part of the “Cuvette Centrale” (Central Basin). This is a large shallow depression composed mainly of dense, humid forest and extending from approximately  $15$ – $25^\circ \text{W}$  and  $5^\circ \text{N}$ – $4^\circ \text{S}$ . Its central western part remains flooded throughout the rainy seasons. Rivers sampled in this region (Sangha, Likouala-aux-Herbes, Likouala, Lengoue, Mambili; Fig. 1, Table 1) drain predominantly sandy or clayey quaternary deposits. The Kouyou Basin (Fig. 1) borders the “Batéké Plateaux”, a  $600$ – $700 \text{ m}$  relief sandstone formation to the south, intersected by dry valleys and covering much of the southern ROC. Here, bushy savannah is intersected by the Alima, Nkény and Léfini rivers. Due to water storage in an underlying sandstone aquifer the hydrological regimes of these three rivers are largely independent of rainfall; they all show only weak seasonality in discharge de-

**Table 1.** Relevant physical characteristics of rivers studied in this work. All rainfall data are from Laraque et al. (2001), Djoue catchment area and discharge data are from Laraque et al. (1994) and all other data are from Laraque et al. (2009).

River/tributary	Catchment area km <sup>2</sup>	Discharge m <sup>3</sup> s <sup>-1</sup>	Rainfall mm
Congo	3 500 000	40 600	1528
Alima	21 030	1941	1709
Nkèni	8000	261	1662
Léfini	14 000	400	1615
Djoue	5740	140	1547
Likouala-aux-Herbes	25 000	267	1622
Sangha	211 120	1941	1511
Likouala Mossaka	69 800	928	1689
Kouyou	16 000	191	1566
Lengoué	12 125	155	
Mambili	13 700	161	
Motaba	772 800	4000	

spite the relatively large variation in monthly precipitation (Laraque et al., 2001).

### 3 Sample collection and analytical techniques

Surface water samples ( $\sim 0.3$  m) were collected from central river channels using a standard “niskin”-type water sampler (<http://www.tresanton.co.uk/standard.html>). We obtained 66 samples for dissolved CH<sub>4</sub>, N<sub>2</sub>O, O<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> analysis, during November 2010 (41 samples) and August 2011 (25 samples; CH<sub>4</sub> and N<sub>2</sub>O only). Based on the monthly rainfall distribution, for convenience we hereinafter refer to these as “wet season” and “dry season” respectively. Samples were slowly decanted into a series of 125 mL glass screw-top septum bottles (Sigma-Aldrich, UK) via a silicon rubber tube. Each was over filled by at least one sample volume to avoid bubble entrainment. Samples were poisoned with 25  $\mu$ L of 0.1 M HgCl<sub>2</sub> to arrest microbial activity and sealed to leave no headspace. They were subsequently returned to Newcastle for dissolved gas analysis within several weeks of collection. Dissolved gas samples treated in this way can be successfully stored for several months (Elkins, 1980).

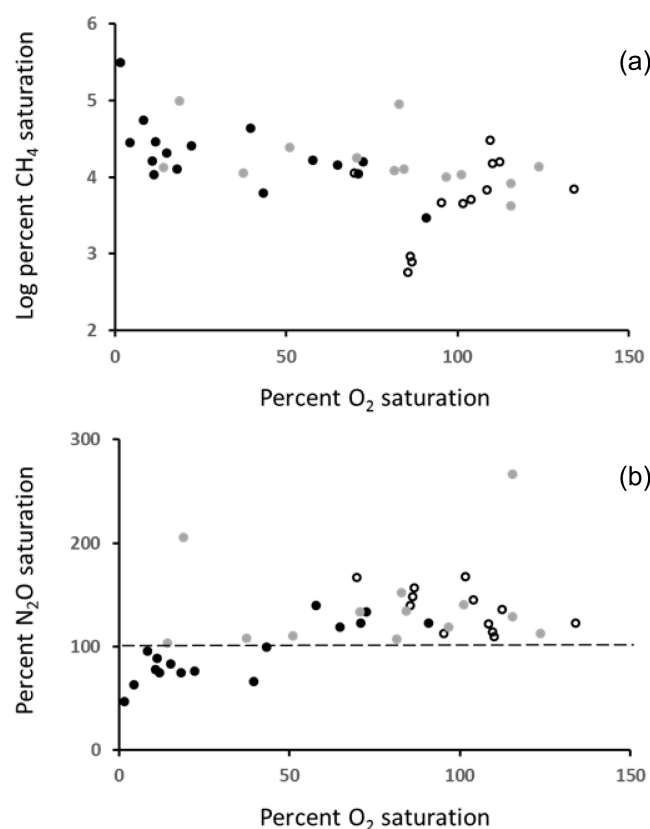
Dissolved CH<sub>4</sub> and N<sub>2</sub>O were analysed by single-phase equilibration gas chromatography (Shimadzu GC 14-B), with flame ionisation detection of CH<sub>4</sub> and electron capture detection of N<sub>2</sub>O (Upstill-Goddard et al., 1996). Routine calibration was with a mixed secondary standard (361 ppbv N<sub>2</sub>O, 2000 ppbv CH<sub>4</sub>) prepared by pressure dilution with ultra-high purity N<sub>2</sub> (Upstill-Goddard et al., 1990). Absolute calibration was against a mixed primary standard (10 ppmv N<sub>2</sub>O, 5 ppmv CH<sub>4</sub>) with a certified accuracy of  $\pm 1$  % (BOC Special Gases, UK). Overall analytical precisions ( $1\sigma$ ) for N<sub>2</sub>O and CH<sub>4</sub>, established via multiple analysis ( $n = 15$ ) of the secondary standard, were both  $\pm 1$  %.

Temperature, dissolved O<sub>2</sub> and atmospheric pressure were measured in situ using a handheld multi-parameter probe (YSI Pro-Plus: <https://www.ysi.com/>). Quoted measurement accuracies are  $\pm 0.2$  °C,  $\pm 2$  % dissolved O<sub>2</sub>, and  $\pm 0.002$  bar. Samples for dissolved NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were filtered on collection (Whatman 0.7  $\mu$ m GF/F; precombusted at 550 °C for 8 h), directly into clean glass vials and stored acidified (pH 2) at 4 °C in the dark for several weeks. Subsequent analysis, at Woods Hole, was by segmented flow (Astoria Analyzer; Astoria-Pacific, USA) using established methods (US Environmental Protection Agency, 1984). Analytical precisions ( $1\sigma$ ) were  $\pm 1$  % for both. Technical and logistical issues precluded the collection of any dissolved O<sub>2</sub>, NH<sub>4</sub><sup>+</sup> or NO<sub>3</sub><sup>-</sup> data during August 2011 (dry season) and some NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> data during November 2010 (wet season).

Emission fluxes,  $F$  (mol m<sup>-2</sup> d<sup>-1</sup>), of CH<sub>4</sub> and N<sub>2</sub>O were estimated using  $F = k_w L \Delta p$ , where  $k_w$  is the transfer velocity of CH<sub>4</sub> or N<sub>2</sub>O (cm hr<sup>-1</sup>),  $L$  is the solubility of CH<sub>4</sub> or N<sub>2</sub>O (mol cm<sup>-3</sup> atm<sup>-1</sup>) (Wiesenburg and Guinasso, 1979; Weiss and Price, 1980) and  $\Delta p$  is the corresponding water-to-air partial pressure difference.  $k_w$  values were derived from two corresponding estimates for CO<sub>2</sub> in the Congo. Raymond et al. (2013) estimated a basin-wide  $k_w$  of 5.2 m d<sup>-1</sup> for CO<sub>2</sub>, using hydraulic equations involving basin slope and flow velocity. The uncertainty in this estimate is  $\sim \pm 10$  % (Raymond et al., 2013). Aufdenkampe et al. (2011) applied constant  $k_w$  values for CO<sub>2</sub> in streams ( $< 100$  m wide: 3.0 m d<sup>-1</sup>) and in rivers ( $> 100$  m wide: 4.2 m d<sup>-1</sup>). Adjusting for the relative areas of these in the Congo Basin (Borges et al., 2015b) gives a basin-wide mean  $k_w \sim 3.9$  m d<sup>-1</sup> for CO<sub>2</sub>. We converted these estimates to  $k_w$  for CH<sub>4</sub> and N<sub>2</sub>O by multiplying by  $(Sc/470.7)^{-0.5}$ , where 470.7 is the Schmidt number of CO<sub>2</sub> in freshwater, and  $Sc$  is the Schmidt number of CH<sub>4</sub> or N<sub>2</sub>O ( $Sc_{CH_4} = 486.8$ ;  $Sc_{N_2O} = 476.9$ ), assuming an ambient temperature of 25 °C (Wanninkhof, 1992). The resulting  $k_w$  estimates are 5.1 and 3.9 m d<sup>-1</sup> for CH<sub>4</sub> and 5.2 and 4.0 m d<sup>-1</sup> for N<sub>2</sub>O. Resulting emissions estimates are consequently  $\sim 30$  % higher based on Raymond et al. (2013). Using both sets of  $k_w$  estimates enables direct comparison with the largest study of CH<sub>4</sub> and N<sub>2</sub>O fluxes for African rivers that also used this approach (Borges et al., 2015b). While other relevant work used wind-speed-based  $k_w$  estimates (Koné et al., 2010; Bouillon et al., 2012) the unavailability of wind speeds precludes their use here. We applied the global mean mixing ratios of CH<sub>4</sub> (1797 ppbv) and N<sub>2</sub>O (323 ppbv) for the year 2010 (<http://cdiac.esd.ornl.gov/tracegases.html>).

### 4 Results

While CH<sub>4</sub> and N<sub>2</sub>O data are available for all samples, dry season data are not available for dissolved O<sub>2</sub>, NO<sub>3</sub><sup>-</sup> or NH<sub>4</sub><sup>+</sup>. Wet season DIN (NO<sub>3</sub><sup>-</sup> + NH<sub>4</sub><sup>+</sup>) is only reported for samples



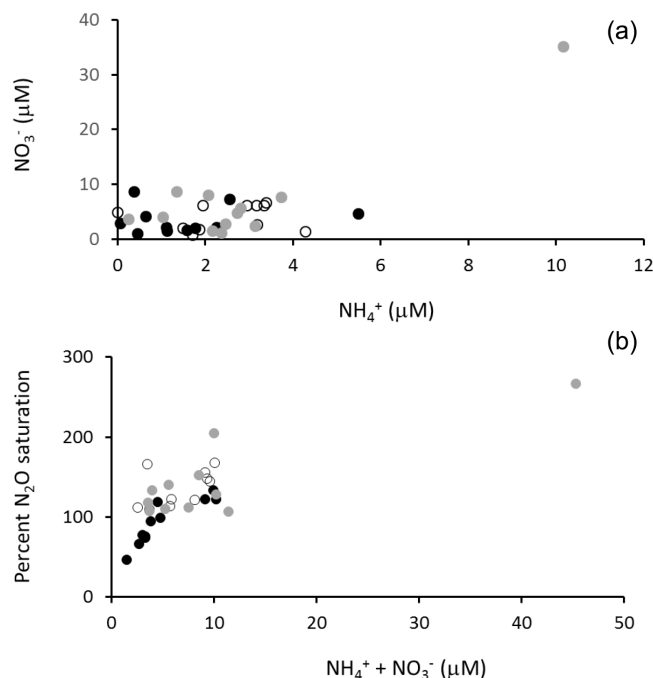
**Figure 2.** (a) Log percent dissolved methane saturation vs. percent dissolved O<sub>2</sub> saturation and (b) percent dissolved nitrous oxide saturation vs. percent dissolved O<sub>2</sub> saturation for rivers of the Republic of Congo during the wet season: open circles, savannah rivers; filled black circles, swamp forest rivers; filled grey circles, tropical forest rivers.

for which both NO<sub>3</sub><sup>−</sup> and NH<sub>4</sub><sup>+</sup> are available. Source data for this paper are available as Supplement (Table S1).

#### 4.1 Dissolved O<sub>2</sub> and DIN

In wet season swamp samples dissolved O<sub>2</sub> varied between mildly undersaturated and very strongly undersaturated (Fig. 2). The mean (36 ± 29 %) and range (4–91 %) of O<sub>2</sub> saturation were both significantly lower than for both forest rivers (Mann–Whitney, one-tailed;  $P = 0.0001$ ) and savannah rivers (Mann–Whitney, one-tailed;  $P = 0.002$ ). Most forest rivers were mildly to strongly O<sub>2</sub> undersaturated (mean 77 ± 36 %, range 14–116 %; Fig. 2) and savannah rivers were predominantly mildly undersaturated to mildly supersaturated (mean 100 ± 17 %, range 70–135 %; Fig. 2).

Low wet season concentrations of dissolved inorganic nitrogen (DIN) components (Fig. 3) are consistent with agricultural, domestic and industrial DIN sources all being negligible (Clark and Decalo, 2012). The means and ranges of total DIN (NO<sub>3</sub><sup>−</sup> + NH<sub>4</sub><sup>+</sup>) did not differ significantly between any of the three



**Figure 3.** (a) Dissolved nitrate vs. dissolved ammonium and (b) percent nitrous oxide saturation vs. DIN (NO<sub>3</sub><sup>−</sup> + NH<sub>4</sub><sup>+</sup>) for rivers of the Republic of Congo during the wet season: open circles, savannah rivers; filled black circles, swamp forest rivers; filled grey circles, tropical forest rivers.

river “types” (mean savannah 6.8 ± 2.8 μmol L<sup>−1</sup>; range 2.5–10.1 μmol L<sup>−1</sup>;  $n = 10$ ; mean swamp 5.1 ± 3.1 μmol L<sup>−1</sup>, range 1.5–10.2 μmol L<sup>−1</sup>;  $n = 11$ ; mean forest 9.4 ± 11.2 μmol L<sup>−1</sup>, range 1.8–45.3 μmol L<sup>−1</sup>;  $n = 12$ ), in contrast to the situation for dissolved O<sub>2</sub>. Differences in NO<sub>3</sub><sup>−</sup>-N were also not significant (mean savannah 4.1 ± 2.3 μmol L<sup>−1</sup>, range 0.8–6.7 μmol L<sup>−1</sup>,  $n = 11$ ; mean swamp 3.6 ± 2.1 μmol L<sup>−1</sup>, range 1.0–8.8 μmol L<sup>−1</sup>,  $n = 16$ ; mean forest 7.1 ± 9.2 μmol L<sup>−1</sup>, range 1.2–35.1 μmol L<sup>−1</sup>;  $n = 12$ ). There was no clear relationship between NO<sub>3</sub><sup>−</sup> and NH<sub>4</sub><sup>+</sup> for any of the three river types (Fig. 3a). NO<sub>3</sub><sup>−</sup> was the dominant DIN component in 24 of the 33 samples for which both NO<sub>3</sub><sup>−</sup> and NH<sub>4</sub><sup>+</sup> were analysed. Considering all samples, the mean NO<sub>3</sub><sup>−</sup> contribution to DIN was 63 ± 19 %.

#### 4.2 Dissolved CH<sub>4</sub> and N<sub>2</sub>O

Table 2 summarises ranges, means and medians of riverine CH<sub>4</sub> and N<sub>2</sub>O concentrations and percent saturations for the three land cover types. All samples were highly CH<sub>4</sub> supersaturated, concentrations spanning two orders of magnitude (11.2–9553 nmol L<sup>−1</sup>; 440–354 400 % saturation). N<sub>2</sub>O spanned a much narrower concentration range and varied from strong undersaturation to strong supersaturation (3.2–20.6 nmol L<sup>−1</sup>; 47–205 %). Evidently, while rivers of the ROC are strong local sources of tropospheric CH<sub>4</sub> they can

act as both small sources and sinks for N<sub>2</sub>O. Swamp rivers exhibited both the lowest and among the highest N<sub>2</sub>O saturations (Table 2) but during the wet season had overall significantly lower N<sub>2</sub>O than either forest or savannah rivers. These were always supersaturated (103–266 %; Table 2) and their overall means and ranges of N<sub>2</sub>O were not significantly different (Mann–Whitney, one-tailed: swamp vs. forest and swamp vs. savannah,  $P = 0.004$ ). For CH<sub>4</sub>, concentration means and ranges during the wet season did not differ significantly between swamp and forest rivers but they were significantly higher in both than in savannah rivers (Mann–Whitney, one-tailed: swamp vs. savannah,  $P = 0.004$ ; forest vs. savannah,  $P = 0.03$ ). In contrast, during the dry season concentration means and ranges of both CH<sub>4</sub> and N<sub>2</sub>O were indistinguishable for all three land cover types. Seasonal differences in concentration means and ranges were not significant for N<sub>2</sub>O for any of the three land cover types or for CH<sub>4</sub> in savannah rivers. In both swamp and forest rivers CH<sub>4</sub> was significantly higher during the wet season (Mann–Whitney, one-tailed: swamp  $P = 0.01$ ; forest  $P = 0.003$ ).

There are comparatively few measurements of CH<sub>4</sub> concentrations in African rivers and even fewer of N<sub>2</sub>O. Our CH<sub>4</sub> data for rivers of the ROC (Table 2) are within the ranges compiled for temperate and tropical rivers (~260–128 000 %) (Upstill-Goddard et al., 2000; Middelburg et al., 2002). Moreover, our CH<sub>4</sub> and N<sub>2</sub>O data both fall within the ranges recently reported for other rivers in sub-Saharan Africa. Studies of CH<sub>4</sub> alone reported 48–870 nmol L<sup>-1</sup> (2221–38 719 % saturation) in three Ivory Coast rivers (Koné et al., 2010), 25–505 nmol L<sup>-1</sup> (850–21 700 % saturation) in the Tana River, Kenya (Bouillon et al., 2009), and 22–71 430 nmol L<sup>-1</sup> in the Congo (Borges et al., 2015a). For concurrent measurements of CH<sub>4</sub> and N<sub>2</sub>O Bouillon et al. (2012) report 74–280 nmol CH<sub>4</sub> L<sup>-1</sup> (3450–13 200 % saturation) and 6.2–9.6 nmol N<sub>2</sub>O L<sup>-1</sup> (112–165 % saturation) in the Oubangui, a major Congo tributary. Teodoru et al. (2015) found 7–12 127 nmol CH<sub>4</sub> L<sup>-1</sup> and 2.0–11.4 nmol N<sub>2</sub>O L<sup>-1</sup> at stations along the Zambezi. Borges et al. (2015b) quote a range of 2–62 966 nmol CH<sub>4</sub> L<sup>-1</sup> (mean: 2205 nmol L<sup>-1</sup>) and 0.2–85.4 nmol N<sub>2</sub>O L<sup>-1</sup> (mean: 9.2 nmol L<sup>-1</sup>) across 12 sub-Saharan river basins, including those of the Congo, Zambezi and Niger.

Considering the complete data set, CH<sub>4</sub> was inversely correlated with both N<sub>2</sub>O and O<sub>2</sub> (Fig. 2). Highest CH<sub>4</sub> coincident with lowest N<sub>2</sub>O and O<sub>2</sub> occurred in swamp rivers. Lowest CH<sub>4</sub> coincident with highest N<sub>2</sub>O and O<sub>2</sub> was observed in forest rivers. Savannah rivers were intermediate between the two (Fig. 2). Overall, log % CH<sub>4</sub> vs. % O<sub>2</sub> showed a weak negative correlation (Fig. 2a;  $R^2 = 0.26$ ,  $n = 41$ ) while % N<sub>2</sub>O vs. % O<sub>2</sub> showed a weak positive correlation (Fig. 2b;  $R^2 = 0.30$ ,  $n = 41$ ). However, for both swamp and forest rivers individually the negative correlations between log % CH<sub>4</sub> and % O<sub>2</sub> were stronger (swamp  $R^2 = 0.38$ ,  $n = 16$ ; forest  $R^2 = 0.45$ ,  $n = 13$ ). While there was a stronger positive correlation between % N<sub>2</sub>O and % O<sub>2</sub> for swamp

**Table 2.** Dissolved CH<sub>4</sub> and N<sub>2</sub>O in Republic of Congo rivers.

Land cover	Date	CH <sub>4</sub> nmol L <sup>-1</sup>			CH <sub>4</sub> saturation %			N <sub>2</sub> O nmol L <sup>-1</sup>			N <sub>2</sub> O saturation %		
		Range	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median
Savannah	All	15–793	204 ± 195	150	571–29 721	7442 ± 73 427	5444	7.6–11.9	8.9 ± 1.1	8.6	6–167	131 ± 19	122
	Wet	15–793	229 ± 141	153	571–29 721	8505 ± 41 111	5936	7.6–11.9	9.1 ± 2.2	9.0	106–167	136 ± 34	137
	Dry	66–243	144 ± 70	150	1660–8717	4888 ± 2878	5444	8.0–9.2	8.4 ± 0.5	8.2	113–130	119 ± 6	117
Swamp	All	17–9553	955 ± 2150	299	659–354 444	35 025 ± 79 578	10 913	3.2–15.3	7.2 ± 2.2	7.2	47–205	101 ± 30	98
	Wet	77–8394	1052 ± 1992	456	2945–309 533	38 485 ± 73 488	16 292	3.2–10.3	6.5 ± 2.1	5.7	47–139	92 ± 28	86
	Dry	17–9553	858 ± 2359	196	659–354 444	31565 ± 87 529	7090	5.3–15.2	7.9 ± 2.2	7.7	78–205	111 ± 29	109
Tropical forest	All	11–2730	551 ± 784	321	440–98 582	16 966 ± 22 958	11 302	7.6–20.6	9.6 ± 3.3	8.4	103–266	135 ± 42	28
	Wet	110–2730	691 ± 852	331	4205–98 582	21 205 ± 24 858	12 729	7.6–20.6	10.0 ± 3.7	5.7	103–266	140 ± 47	128
	Dry	11–232	94 ± 103	67	440–82 183	3319 ± 3360	2310	8.0–8.5	8.3 ± 0.2	8.3	108–232	120 ± 12	120



rivers than for the complete data set ( $R^2 = 0.71$ ,  $n = 16$ ), the correlation for forest rivers was extremely weak ( $R^2 = 0.02$ ,  $n = 13$ ). For savannah rivers we found a positive correlation between  $\log \% \text{CH}_4$  and  $\% \text{O}_2$  ( $R^2 = 0.23$ ;  $n = 12$ ) and a negative correlation between  $\% \text{N}_2\text{O}$  and  $\% \text{O}_2$  ( $R^2 = 0.35$ ,  $n = 12$ ).  $\text{N}_2\text{O}$  co-varied positively with both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  (Fig. 3). For the complete data set the correlations were weak ( $\text{N}_2\text{O}$  vs.  $\text{NO}_3^-$ ,  $R^2 = 0.28$ ,  $n = 59$ ;  $\text{N}_2\text{O}$  vs.  $\text{NH}_4^+$ ,  $R^2 = 0.23$ ,  $n = 40$ ). For all three river types individually, with the exception of  $\text{N}_2\text{O}$  vs.  $\text{NH}_4^+$  in savannah rivers, the correlations were stronger, and for all rivers  $\text{NO}_3^-$  was a stronger predictor of  $\text{N}_2\text{O}$  ( $\text{N}_2\text{O}$  vs.  $\text{NO}_3^-$ :  $R^2$  swamp = 0.50,  $n = 29$ ;  $R^2$  forest = 0.75,  $n = 15$ ;  $R^2$  savannah = 0.31,  $n = 15$ ) than was  $\text{NH}_4^+$  ( $\text{N}_2\text{O}$  vs.  $\text{NH}_4^+$ :  $R^2$  swamp = 0.29,  $n = 13$ ;  $R^2$  forest = 0.47,  $n = 13$ ;  $R^2$  savannah = 0.01,  $n = 14$ ).

### 4.3 CH<sub>4</sub> and N<sub>2</sub>O emission fluxes

Table 3 summarises ranges, means and medians of CH<sub>4</sub> and N<sub>2</sub>O emission fluxes using  $k_w$  derived from Raymond et al. (2013) and Aufdenkampe et al. (2011). Fluxes broadly followed the distribution of concentrations. CH<sub>4</sub> fluxes were lowest overall in savannah rivers and highest in swamp and forest rivers. N<sub>2</sub>O fluxes were lowest in swamp rivers and highest in savannah and forest rivers. Fluxes were always to air at all sites for CH<sub>4</sub> and at all savannah and forest sites for N<sub>2</sub>O. However, swamp rivers were predominantly a N<sub>2</sub>O sink during the wet season (11 of 16 individual flux estimates) and predominantly a N<sub>2</sub>O source during the dry season (10 of 16 individual flux estimates). As far as we are aware the wet season sink for N<sub>2</sub>O in swamp rivers is the first such reported for African rivers.

## 5 Discussion

### 5.1 Sources of CH<sub>4</sub> and N<sub>2</sub>O

The concentrations of dissolved CH<sub>4</sub> and N<sub>2</sub>O at any specified river location reflect a dynamic and complex balance. This involves in situ production and consumption impacted by import and export mechanisms that include upstream and downstream advection, groundwater inputs, local surface runoff and water–air exchange.

While dissolved O<sub>2</sub> was undersaturated in the majority of samples, being as low as 4 % in one wet season swamp sample, it was always detectable and indeed was supersaturated in several savannah river samples in which CH<sub>4</sub> saturations ranged from  $\sim 4000$  to 10 000 % (Fig. 2a). Notwithstanding that methanogenesis is an exclusively anoxic process carried out by severely O<sub>2</sub>-limited archaea (Bridgman et al., 2013), the existence of high CH<sub>4</sub> concentrations in oxygenated rivers is well known (e.g. Richey et al., 1988). It is a consequence of the diffusion of CH<sub>4</sub> produced in underlying river sediments, in adjacent floodplain soils and in adjacent

**Table 3.** Emissions of CH<sub>4</sub> and N<sub>2</sub>O to air from rivers in the Republic of Congo. Negative values in parentheses indicate uptake from the atmosphere.

Land cover	Date	CH <sub>4</sub> emission flux (μmol m <sup>-2</sup> d <sup>-1</sup> )			N <sub>2</sub> O emission flux (μmol m <sup>-2</sup> d <sup>-1</sup> )								
		Raymond et al. (2013)	Aufdenkampe et al. (2011)		Raymond et al. (2013)	Aufdenkampe et al. (2011)							
Savannah	All	61–4030	1027 ± 997	752	43–3081	785 ± 762	575	3–25	11 ± 7	8	3–19	8 ± 5	6
	Wet	61–4030	1159 ± 1157	876	47–3081	887 ± 885	670	3–25	12 ± 7	13	3–19	9 ± 5	10
	Dry	321–855	595 ± 396	602	245–654	455 ± 272	460	5–11	7 ± 2	6	4–8	5 ± 2	5
Swamp	All	74–48 705	4856 ± 10 964	1512	56–37 245	3713 ± 8384	1196	(–19)–41	1 ± 11	(–1)	(–15)–31	1 ± 9	(–1)
	Wet	378–42 798	5349 ± 10 160	2313	289–32 728	4090 ± 7767	1767	(–19)–15	(–3) ± 10	(–5)	(–15)–12	(–2) ± 8	(–4)
	Dry	74–48 705	4363 ± 12 029	985	56–37 245	3336 ± 9198	753	(–8)–41	4 ± 11	3	(–6)–31	3 ± 9	3
Tropical forest	All	43–13 911	2795 ± 4000	1624	33–10 638	2318 ± 3059	1242	1–67	13 ± 16	9	1–51	10 ± 13	7
	Wet	549–13 911	3512 ± 4387	1677	420–10 638	2686 ± 3324	1282	1–67	15 ± 19	10	1–51	11 ± 14	7
	Dry	43–11 67	465 ± 526	326	33–892	356 ± 403	249	3–11	7 ± 3	7	3–8	15 ± 3	5



wetlands, into aerated river water. Previous work showed that the CH<sub>4</sub> supply from groundwater to African rivers is generally comparatively low (Balagizi et al., 2015; Borges et al., 2015b). The spatial distribution of dissolved CH<sub>4</sub> is more closely related to the wetland distribution within the catchment, wetland water deriving principally from upland runoff (Borges et al., 2015a). In the Congo Basin floating macrophytes, both in the centre of river channels and fringing their edges, are important additional sources of CH<sub>4</sub> (Borges et al., 2015a). These sources promote a unidirectional CH<sub>4</sub> flow, towards small and large river channels (Borges et al., 2015a). Where these river channels are shallow and have low levels of surface turbulence, as in the examples studied here, the CH<sub>4</sub> diffusion term evidently exceeds combined CH<sub>4</sub> losses via oxidation and water-to-air exchange. This further promotes the accumulation of high river CH<sub>4</sub> concentrations.

In addition to methanogenesis in fully anoxic sediment and soils, CH<sub>4</sub> production can also occur in “anoxic microsites” within oxic soils (e.g. Teh et al., 2005; von Fisher and Hedin, 2007). Indeed, methanogens are now considered to be widespread in oxic soils and they are activated during flooding (Bridgham et al., 2013). Their activity relates to soil carbon age and composition (Bridgham et al., 1998; Chanton et al., 2008) and likely involves substrate competition and other interactions. Production by soil macrofauna (Kammann et al., 2009), archeal production related to plant productivity (Updegraff et al., 2001; Dorodnikov et al., 2011) and non-microbial, direct aerobic production, both by living plant tissue (Keppler et al., 2006, 2009) and in soils (Hurkuck et al., 2012), have all also been observed. Although methanogenesis by photoautotroph-attached archaea has been detected in oxic lake water (Grossart et al., 2011) this is unlikely in tributaries and wetlands of the Congo, where phytoplankton abundance is low (Descy et al., 2016). Additional to this variability in production mechanisms and rates, CH<sub>4</sub> is subject to variable and rapid aerobic and anaerobic microbial oxidation (Megonigal et al., 2004). Oxidative CH<sub>4</sub> loss rates have been variously estimated at between a few percent and > 100 % of the rate of methanogenesis (Bussmann, 2013; Shelley et al., 2015). Despite such potentially high losses, water to air exchange by ebullition and by turbulent diffusion driven by wind stress, water depth and flow velocity (Raymond and Cole, 2001) is usually considered the major CH<sub>4</sub> loss term, with ebullition frequently considered the dominant of these two mechanisms (Stanley et al., 2016). Despite this complexity of dissolved CH<sub>4</sub> cycling in rivers, it is nevertheless informative to speculate on our principal observations in the context of potential CH<sub>4</sub> sources and sinks.

The first notable feature of our results is the contrasting relationship between CH<sub>4</sub> and O<sub>2</sub> in swamp and forest rivers (negative) and in savannah rivers (positive) (Fig. 2a). Dissolved O<sub>2</sub> in rivers is primarily driven by the balance of photosynthesis and respiration (Houser et al., 2015). It may be additionally impacted by varying contributions from water–air exchange that under conditions of extreme turbulence

may lead to supersaturations as high as 150 % (Li et al., 2010). The overall positive relationship between CH<sub>4</sub> and O<sub>2</sub> in savannah rivers (Fig. 2a) could, at least in part, reflect high macrophyte-related productivity. This can give rise to positive relationships by direct CH<sub>4</sub> production (Stanley et al., 2016) and by indirect production via the trapping of fine-grained organic sediments that support methanogenesis (Sanders et al., 2007). Similar relationships were observed in Amazon floodplain lakes (Devol et al., 1990). Offsetting this, stems and roots respire O<sub>2</sub> (Caraco et al., 2006). Further inspection of the data shows that the highest dissolved O<sub>2</sub> saturation found in savannah rivers (134 %) deviates from the general CH<sub>4</sub> vs. O<sub>2</sub> trend (Fig. 2a). This sample was collected close to an area of rapids in the Congo main stem, in the vicinity of Pool Malebo (formerly known as Stanley Pool) (Fig. 1) where other samples were also O<sub>2</sub> supersaturated. Intense water–air exchange in this region via increased turbulence would tend to enhance dissolved O<sub>2</sub> (Li et al., 2010) while depleting dissolved CH<sub>4</sub>. To summarise, notwithstanding possible additional CH<sub>4</sub> losses via oxidation, the CH<sub>4</sub> vs. O<sub>2</sub> relationship in savannah rivers (Fig. 2a) could be explained by net macrophyte production imprinted by water–air gas exchange. The inverse of this relationship for swamp and forest rivers (Fig. 2a) was similarly reported for the Zambezi and Amazon basins, for the latter in fast flowing waters (Teodoru et al., 2015; Richey et al., 1988; Devol et al., 1990). Again, high gas exchange rates are plausible, especially for the small number of tropical forest samples for which O<sub>2</sub> was close to or in excess of 100 % (Fig. 2a). For the majority of samples that were O<sub>2</sub> undersaturated, however, additional mechanisms must be invoked. One possibility is that these distributions largely reflect the mixing of relatively well-oxygenated river waters with high-CH<sub>4</sub>, low-O<sub>2</sub> groundwater but another possibility is that this relationship is the aggregate of this and several of the other processes previously discussed.

A second important aspect of the overall CH<sub>4</sub> distributions is that swamp and forest river CH<sub>4</sub> was highest during the wet season, whereas savannah samples revealed no such inter-seasonal contrast (Table 2). The constancy of CH<sub>4</sub> in savannah rivers might well reflect the buffering of seasonal river discharge by the sandstone aquifer that underlies this region (Laraque et al., 2001). For swamp and forest rivers a number of alternative but not mutually exclusive possibilities might be invoked. In addition to direct and indirect macrophyte production (Stanley et al., 2016; Sanders et al., 2007), as discussed for savannah rivers, methanogenesis following the activation of archaea during flooding of adjacent soils (Bridgham et al., 2013) is also plausible. This is supported by the observation that swamp and forest soils are comparatively poorly drained (Mayaux et al., 2002). In contrast, an opposing behaviour was reported for three rivers of the Ivory Coast (Comoé, Bia, Tanoé). In these, overall decreases in CH<sub>4</sub> during the dry to wet season transition (Koné et al., 2010) were similar to trends recorded in some temperate (Eu-

**Table 4.** Emissions of CH<sub>4</sub> and N<sub>2</sub>O published for African rivers: (A) refers to emissions estimated using the relationship of Aufdenkampe et al. (2011) and (R) refers to emissions estimated using the relationship of Raymond et al. (2013).

River	CH <sub>4</sub> emission flux ( $\mu\text{mol m}^{-2} \text{d}^{-1}$ )		N <sub>2</sub> O emission flux ( $\mu\text{mol m}^{-2} \text{d}^{-1}$ )		Reference
	Range	Mean	Range	Mean	
Conoé, Ivory Coast		288 ± 107			Koné et al. (2010)
Bia, Ivory Coast		155 ± 38			Koné et al. (2010)
Tanoé, Ivory Coast		241 ± 91			Koné et al. (2010)
Ivory Coast (all)	25–1187				Koné et al. (2010)
Oubangui	38–350		0.6–5.7		Bouillon et al. (2012)
Congo		14 296		15 (A)	
		18 534		19 (R)	Borges et al. (2015b)
Ivory Coast		1003		(A)	
		1667		(R)	Borges et al. (2015b)
Ogooué		2115		13 (A)	
		4668		28 (R)	Borges et al. (2015b)
Niger		502		4 (A)	
		583		5 (R)	Borges et al. (2015b)
Zambezi		8348		2 (A)	
		13 597		2 (R)	Borges et al. (2015b)
Betsiboka		1305		4 (A)	
		3493		9 (R)	Borges et al. (2015b)
Rianala		1923		5 (A)	
		4537		12 (R)	Borges et al. (2015b)
Tana		568		6 (A)	
		604		6 (R)	Borges et al. (2015b)
Athi-Galana-Sabaki		1156		16 (A)	
		1374		19 (R)	Borges et al. (2015b)
Nyong		18019		(A)	
		28579		(R)	Borges et al. (2015b)

ropean) rivers (Middelburg et al., 2002). Koné et al. (2010) ascribed the CH<sub>4</sub> seasonality in Ivory Coast rivers to a combination of the dilution of high-CH<sub>4</sub> baseflow by low-CH<sub>4</sub> surface runoff (e.g. Jones and Mulholland, 1998a, b), higher degassing rates during flooding (Hope et al., 2001) and/or decreased in-stream methanogenesis towards high discharge (De Angelis and Scranton, 1993). Conversely, Bouillon et al. (2012) attributed relatively stable high-discharge CH<sub>4</sub> concentrations ( $\sim 100 \text{ nmol L}^{-1}$ ) in the Oubangui, a major tributary of the Congo, to terrestrial soil production in conjunction with baseflow transport. The largest fractional CH<sub>4</sub> contribution from baseflow often occurs in high elevation headwaters with high soil organic content, while progressive downstream increases in CH<sub>4</sub> in lowland rivers have been linked to increasing in-stream methanogenesis (Jones and Mulholland, 1998a). Assuming such processes are also operative in ROC swamp and tropical forest, interpreting or predicting the direction of any seasonal CH<sub>4</sub> trend in a specified river system is evidently complex.

In contrast to CH<sub>4</sub>, natural sources of aquatic N<sub>2</sub>O are entirely microbial, and involve several pathways. Nitrification is a two-stage process in which NH<sub>4</sub><sup>+</sup> is first oxidised aerobically to NO<sub>2</sub><sup>−</sup> via hydroxylamine (NH<sub>2</sub>OH),

followed by NO<sub>2</sub><sup>−</sup> oxidation to NO<sub>3</sub><sup>−</sup>. Following the first stage, N<sub>2</sub>O can be produced through various routes: nitrifier nitrification (NH<sub>2</sub>OH → N<sub>2</sub>O), nitrifier denitrification (NO<sub>2</sub><sup>−</sup> → NO → N<sub>2</sub>O) and nitrification-coupled denitrification (NO<sub>3</sub><sup>−</sup> → NO<sub>2</sub><sup>−</sup> → NO → N<sub>2</sub>O) (Kool et al., 2011). Heterotrophic denitrification, in which NO<sub>3</sub><sup>−</sup> is the terminal electron acceptor (NO<sub>3</sub><sup>−</sup> → NO<sub>2</sub><sup>−</sup> → NO + N<sub>2</sub>O → N<sub>2</sub>), occurs in soils, sediments and waters that are anoxic, the inhibition of denitrifier activity at very low levels of dissolved O<sub>2</sub> being well known (Knowles, 1982). Even so, in the complete absence of O<sub>2</sub>, N<sub>2</sub>O can be enzymatically reduced to gaseous N<sub>2</sub> (Wrage et al., 2001), both in sediments and in the water column, sometimes resulting in extreme N<sub>2</sub>O undersaturations (Nirmal Rajkumar et al., 2008).

Although we found no statistically significant differences in the means and ranges of wet or dry season N<sub>2</sub>O concentrations for any land cover type, higher N<sub>2</sub>O concentrations and emissions are considered likely where soil-water-filled pore spaces exceed 60 % due to enhanced microbial production (Davidson, 1993). This has been observed in African savannah during the rainy season (Castaldi et al., 2006) and throughout much of the year in humid tropical forests

(Castaldi et al., 2013). The discrepancy between these and our observations to some extent likely reflects a complex balance between the principal sites (groundwater and in-stream) and mechanisms of N<sub>2</sub>O cycling, as evidenced by the variable relationships between N<sub>2</sub>O, O<sub>2</sub> and DIN we observed. For example, we found both positive and negative relationships between N<sub>2</sub>O and O<sub>2</sub> (Fig. 2b). Sediment processes and water concentrations are evidently closely coupled in tropical catchments (Harrison and Matson, 2003). A strong positive correlation between N<sub>2</sub>O and O<sub>2</sub> in swamp rivers coincident with strong undersaturation of both N<sub>2</sub>O and O<sub>2</sub> (Fig. 2b) is consistent with N<sub>2</sub>O consumption by sediment denitrification. Positive relationships between N<sub>2</sub>O and NO<sub>3</sub><sup>−</sup> have been variously interpreted to reflect nitrification (Silvennoinen et al., 2008; Beaulieu et al., 2010), or both denitrification and nitrification (Baulch et al., 2011). Even so, for swamp rivers the stronger correlation between N<sub>2</sub>O and NO<sub>3</sub><sup>−</sup> than between N<sub>2</sub>O and NH<sub>4</sub><sup>+</sup>, which is often taken to indicate a sediment denitrification N<sub>2</sub>O source (Dong et al., 2004), supports our conclusion of a swamp river denitrification sink for N<sub>2</sub>O. Similar N<sub>2</sub>O vs. O<sub>2</sub> relationships were identified in the Amazon and Zambezi river basins (Richey et al., 1988; Teodoru et al., 2015) and in the Adyar river estuary, southeastern India (Nirmal Rajkumar et al., 2008). In both the Amazon and the Adyar, N<sub>2</sub>O was undetectable in fully anoxic waters (Richey et al., 1998; Nirmal Rajkumar et al., 2008). N<sub>2</sub>O and NO<sub>3</sub><sup>−</sup> were also correlated in the Oubangui (Bouillon et al., 2015b) and in several other African rivers (Borges et al., 2015b). A similar, persistent correlation in a temperate river was ascribed to denitrification in hypoxic/anoxic sediment, favoured by the ambient low river flow and high temperatures leading to high community respiration and low O<sub>2</sub> solubility (Rosamond et al., 2012). Even though denitrification in rivers may be limited by low levels of NO<sub>3</sub><sup>−</sup> (Garcia-Ruiz et al., 1998) a temperate creek was a N<sub>2</sub>O sink for combined NO<sub>2</sub><sup>−</sup> and NO<sub>3</sub><sup>−</sup> concentrations < 2.7 μmol L<sup>−1</sup> (Baulch et al., 2011), broadly similar to the majority of NO<sub>3</sub><sup>−</sup> concentrations we observed (Fig. 3a). By contrast, N<sub>2</sub>O and NO<sub>3</sub><sup>−</sup> were uncorrelated in the Zambezi, for which there was also no correlation of N<sub>2</sub>O with NH<sub>4</sub><sup>+</sup> (Teodoru et al., 2015). For savannah rivers, in which N<sub>2</sub>O was always supersaturated (Fig. 2b), a negative correlation between N<sub>2</sub>O and O<sub>2</sub> may indicate N<sub>2</sub>O production mainly by nitrification. This is supported by the corresponding stronger correlation between N<sub>2</sub>O and NH<sub>4</sub><sup>+</sup> than between N<sub>2</sub>O and NO<sub>3</sub><sup>−</sup>, the opposite to what we found for swamp rivers. Although published measurements of N<sub>2</sub>O production via in-stream nitrification are lacking, nitrification rates may frequently exceed denitrification rates in streams and rivers (Richardson et al., 2004; Arango et al., 2008) and nitrification rates are estimated to exceed denitrification rates 2-fold globally (Mosier et al., 1998). In addition to O<sub>2</sub> and DIN amount and speciation, pH and dissolved organic carbon are important in controlling net N<sub>2</sub>O production via nitrification and denitrification (Baulch et al., 2011).

It has been suggested that, due to variable N<sub>2</sub>O yields from these processes, simple diagnostic relationships for N<sub>2</sub>O production in rivers may prove elusive (Beaulieu et al., 2008).

In summary, our data have allowed us to draw some conclusions regarding the production and cycling of CH<sub>4</sub> and N<sub>2</sub>O in contrasting rivers of the ROC. However, for both gases an unequivocal identification of the primary controls of their riverine distributions would require additional detailed measurements.

## 5.2 CH<sub>4</sub> and N<sub>2</sub>O emissions in the wider context

As with the concentration measurements, there are few data for African rivers with which to compare our CH<sub>4</sub> and N<sub>2</sub>O emissions estimates (Table 3). Previously published emissions estimates are listed in Table 4. For three rivers of the Ivory Coast Koné et al. (2010) report 25 to 1187 μmol CH<sub>4</sub> m<sup>−2</sup> d<sup>−1</sup>, while for the Oubangui Bouillon et al. (2012) found 38 to 350 μmol CH<sub>4</sub> m<sup>−2</sup> d<sup>−1</sup> and 0.6 to 5.7 μmol N<sub>2</sub>O m<sup>−2</sup> d<sup>−1</sup>. For 12 sub-Saharan African rivers Borges et al. (2015b) give ranges of 0 to 274 600 mmol CH<sub>4</sub> m<sup>−2</sup> d<sup>−1</sup> and −30 to 299 mmol N<sub>2</sub>O m<sup>−2</sup> d<sup>−1</sup> using *k<sub>w</sub>* from Aufdenkampe et al. (2011), and 0 to 461 967 mmol CH<sub>4</sub> m<sup>−2</sup> d<sup>−1</sup> and −37 to 377 mmol N<sub>2</sub>O m<sup>−2</sup> d<sup>−1</sup> using *k<sub>w</sub>* from Raymond et al. (2013). For comparison, CH<sub>4</sub> emissions estimated for the Amazon River were 4625 to 12 562 μmol m<sup>−2</sup> d<sup>−1</sup> (Bartlett et al., 1990) and the range for CH<sub>4</sub> in temperate rivers is ~0 to 22000 μmol m<sup>−2</sup> d<sup>−1</sup> (De Angelis and Scranton, 1993; Lilley et al., 1996; Jones and Mulholland, 1998a, b; Hope et al., 2001; Abril and Iversen, 2002). Guérin et al. (2008) reported N<sub>2</sub>O emissions ~0.25 to 6.0 μmol m<sup>−2</sup> d<sup>−1</sup> for the Amazon River and floodplain, while Soued et al. (2016) found N<sub>2</sub>O fluxes in Canadian boreal rivers to be highly variable across ecosystem types and seasons. These ranged from net uptake ~3.3 μmol m<sup>−2</sup> d<sup>−1</sup>, somewhat lower than the maximum N<sub>2</sub>O uptake we observed in swamp rivers (Table 3), to net emissions ~4.8 μmol m<sup>−2</sup> d<sup>−1</sup>.

The overall ranges of CH<sub>4</sub> and N<sub>2</sub>O emissions from rivers of the ROC (33 to 48 705 mmol CH<sub>4</sub> m<sup>−2</sup> d<sup>−1</sup>; 1 to 67 mmol N<sub>2</sub>O m<sup>−2</sup> d<sup>−1</sup>, Table 3) fall within the ranges encompassed by these earlier estimates for African and temperate rivers. It should be acknowledged that the use of “basin-wide” values for *k<sub>w</sub>* is a necessity that takes no account of spatial and temporal *k<sub>w</sub>* variability, that our emissions based on *k<sub>w</sub>* derived from Raymond et al. (2013) are 30 % higher than those derived from Aufdenkampe et al. (2011) and that other available *k<sub>w</sub>* parameterisations show 5-fold variability (Barnes and Upstill-Goddard, 2011). Additionally, we did not measure CH<sub>4</sub> ebullition fluxes. Borges et al. (2015b) report an average 20 % ebullition contribution to total CH<sub>4</sub> emissions from the Congo and Zambezi, although their maximum estimates are considerably higher than this. For some other tropical rivers and lakes ebullition is thought to account for 30–98 % of total CH<sub>4</sub> emissions (Melack et al., 2004; Bastviken

et al., 2011; Sawakuchi et al., 2014). The uncertainties related to  $k_w$  notwithstanding, our emissions estimates for CH<sub>4</sub>, at least, are therefore probably conservative.

## 6 Conclusions

Our data from the ROC support the growing consensus that river systems in Africa may be disproportionately large contributors to the global freshwater sources of tropospheric CH<sub>4</sub> and N<sub>2</sub>O, as they are for CO<sub>2</sub>. Even so, the potential for significant sinks lends a note of caution for N<sub>2</sub>O. The wide ranges of emissions estimates for CH<sub>4</sub> and N<sub>2</sub>O now available for African rivers clearly illustrate the difficulty in deriving representative total emissions given both the comparatively small size of the available data set and the various approaches that are typically used to derive these emissions. This applies not only to African rivers but to tropical rivers in general and indeed to freshwaters globally. At least equally important is an insufficiently mature understanding of the processes that link emissions to the environmental controls of process rates and their temporal variability, and to river catchment characteristics that include sources and seasonality of organic inputs and variability in the balance between baseflow and surface runoff. Our understanding of these interactions must improve if the system responses to future climate and land use changes are to be predicted and planned for. Lastly, the measurement of CH<sub>4</sub> and N<sub>2</sub>O, data calibration and the emissions estimates for aquatic systems deriving would all benefit from agreed, standardised protocols. There are currently no internationally agreed calibration standards for CH<sub>4</sub> or N<sub>2</sub>O, but this is now being addressed via an international SCOR (Scientific Committee on Oceanic Research) working group (WG-143: <https://portal.geomar.de/web/scor-wg-143/home>), which is engaged in inter-laboratory calibration and the dissemination of high quality calibration gases. WG-143 welcomes additional interest from the wider aquatic CH<sub>4</sub> and N<sub>2</sub>O research community.

**Data availability.** All available data for this project are in the accompanying on-line supplement.

**The Supplement related to this article is available online at doi:10.5194/bg-14-2267-2017-supplement.**

**Competing interests.** The authors declare that they have no conflict of interest.

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